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Delivery Order 0044: Accelerated Computational Approach to Multi-scale Relaxation in Nanoparticulate-polymer Composites

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14. ABSTRACT
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 1 December 2005 through 1 April 2008. This task developed and validated Monte Carlo computational methods for the modeling of two-dimensional nanoplates in polymer/solvent matrix. Nano-particulate polymer composites consist of multi-component systems with such constituents as solvent, polymer chains, clay platelets etc. The vast parameter space includes molecular weight of constituents, their concentrations, temperature, and interaction apart from processing and driving mechanism (shearing, compression, etc.). The constitutive components can be described by particles, chains, and sheets in a coarse-grained modeling by computer simulations. Relaxation of each component and their cooperative dynamics lead to multi-scale responses resulting in self-organizing structures. While the stochastic dynamics of each component facilitate equilibration, the physical entanglement, local-crowding, and jamming cause entropic constraints that may hinder thermal equilibration. The evolving structure may or may not be in thermodynamics equilibrium depending on the time scales. Understanding the structure and dynamics of such a multi-component system is known for its complexities. Therefore, we proposed to address some of the issues by accelerated computational approach.

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An Accelerated Computational Approach To Multi-Scale Relaxation In Nano-Particulate-Polymer Composites

Alan T. Yeates[1], Ras B. Pandey[2], Barry L. Farmer[1]

Nano-particulate polymer composites[1] consist of multi-component systems with such constituents as solvent, polymer chains, clay platelets etc. The vast parameter space includes molecular weight of constituents, their concentrations, temperature, and interaction apart from processing and driving mechanism (shearing, compression, etc.). The constitutive components can be described by particles, chains, and sheets in a coarse-grained modeling by computer simulations. Relaxation of each component and their cooperative dynamics lead to multi-scale responses resulting in self-organizing structures. While the stochastic dynamics of each component facilitate equilibration, the physical entanglement, local-crowding, and jamming cause entropic constraints that may hinder thermal equilibration. The evolving structure may or may not be in thermodynamics equilibrium depending on the time scales. Understanding the structure and dynamics of such a multi-component system is known for its complexities. Therefore, we proposed to address some of the issues by accelerated computational approach.

Model: We use discrete lattice with ample degrees of freedom to develop an efficient computer simulation model. Particle is represented by a unit cell of the lattice. Chains and sheets are designed from tethering particles/nodes in a linear chain and two-dimensional network respectively. Conformation and dynamics of polymer chains have been studied for a long time[2,3]; advantages and pitfall of models, approaches, and computational methods have been extensively examined[1]. Using the vast amount of knowledge gained from the computer simulation modeling of polymer chains over several decades[2], we have successfully developed a model for the flexible sheet[4,5]. If particle to chain is a large jump in complexity in regard to both structure and dynamics of the underlying polymer system, extending the modeling from a chains to a sheet is even more complex. The idea of bond-fluctuating sheet on a discrete lattice, analogous to a bond-fluctuating chain is a major contribution to a set of basic components (particle, and chain) in modeling composites and the starting point of our investigations[4,5]. Attempts are made to understand the fundamental properties of sheet and dispersion of layered platelets in solvent and polymer matrix systematically using Monte Carlo simulations on a cubic lattice of size L^3. In the following, we briefly describe main results from our investigations.

A platelet (sheet) is described[4,5] by a set of L_s^2 nodes tethered together by flexible bonds on a cubic lattice (see Figure 1); the distance between the nearest neighbor nodes is twice the lattice constant, the minimum bond length. A node is represented by a unit cube (i.e., eight sites) of the lattice. Since a lattice site cannot be occupied by more than one node due to excluded volume constraints, the minimum distance between consecutive tethered nodes, (i.e. the bond length) is two in units of the lattice constant. The bond length can fluctuate between *2* and *√10* with an exception of *√8* as the node attempts to move stochastically (see below) to one of its *26*

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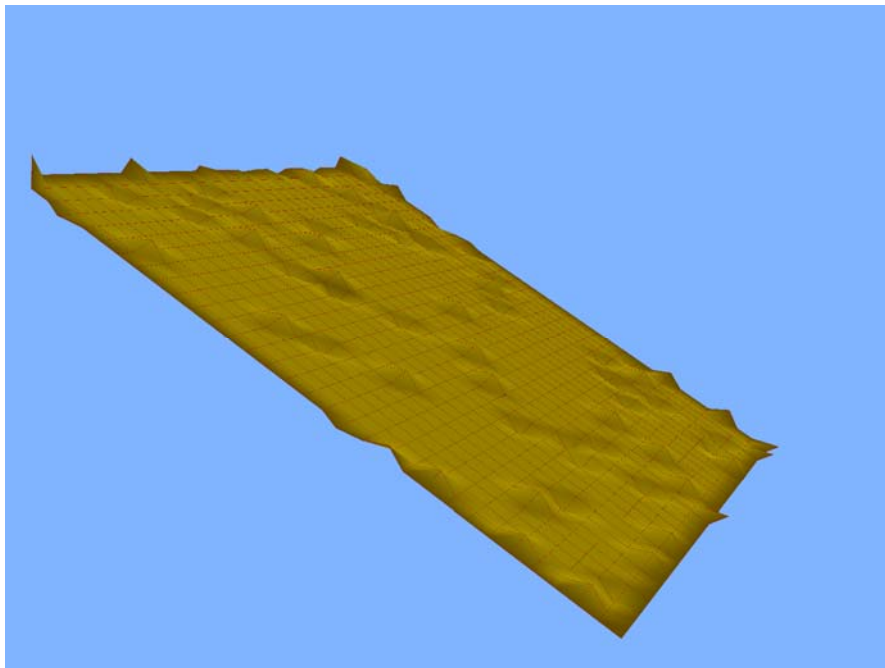adjacent cubes (referred as sites in the following description) similar to the bond-fluctuation model for a polymer chain[2].

Figure 1. Representation of a Square Sheet.

The interaction energy of a node is described by,

$$E = \sum_{ij} J(i,j),$$

where i runs over each node and j over neighboring sites within a range r. It should be pointed out that the range r should be large enough to incorporate appropriate constituents (platelet nodes and solvent particles) in the local vicinity of a node. For example, the minimum value of r must be 2 to reach a nearest node in a sheet; typically $r^2 = 6, 8$. The empty lattice sites may constitute an effective medium. Different types of node-node interaction ($J(n,n) = \varepsilon_{nn}$) and node-solvent interaction ($J(n,n) = \varepsilon_{ns}$) can be considered within a range (r) which can be varied. The sheet is also referred as tethered membrane which exhibits unique conformational characteristics as it wrinkles and crumples under various conditions (quality of solvent, entropic constraints due to presence of polymer chains, temperature, etc.) while entropy dissipates from its open boundary.

As the nodes execute their stochastic motion, the conformation of the sheet relaxes and approaches its equilibrium value. Relaxation of the radius of gyration (Figure 2) is examined in detail along with its dependence on the temperature (Figure 3). Depending on the node-node interaction (attractive, repulsive), Figure 2 shows how a sheet expands (repulsive) or shrinks (attractive) at low and high temperatures. Our simulations also predict how the radius of gyration varies with the temperature[5, 6] (see Figure 3). Since the simulations take relatively long time for larger sheets to equilibrate, these studies are limited to few temperatures with the larger sheets. However, the trend in temperature dependence of the radius of gyration with the smaller sheet seems to provide reliable insight into the qualitative picture.
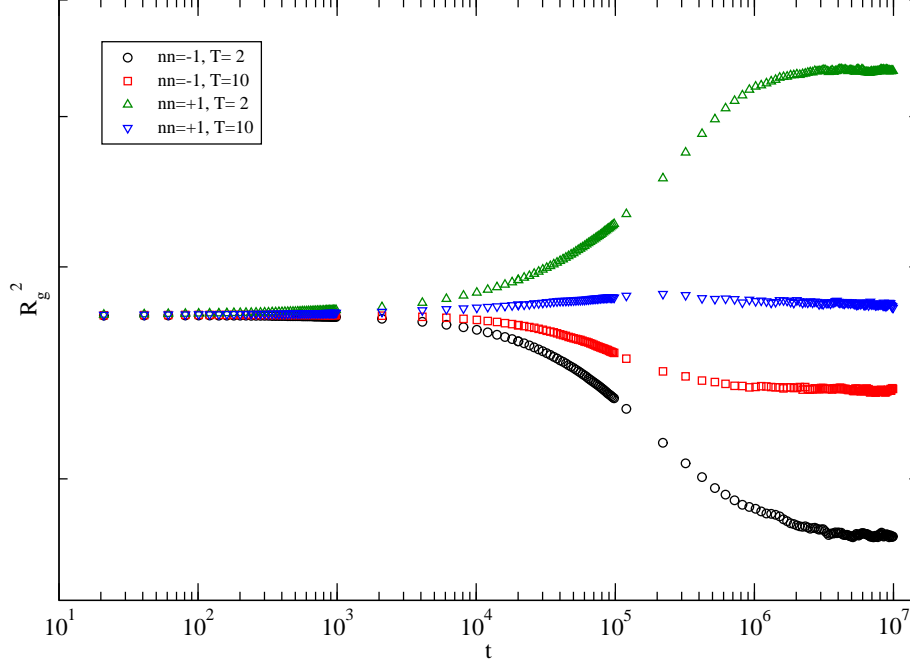
Figure 2. **Variation of the mean square radius of gyration (R_g^2) of the sheet (64^2) with the time step (t) on a 200^3 lattice with the node-node interaction $nn = -1, 1$ and node-solvent interaction $ns = -0.5$ at temperature $T = 2, 10$. 10-1000 independent samples are used. Ref [6].**

Stochastic dynamics of a node (particle) in a free polymer chain describes short to long time characteristics, e.g., short time Rouse dynamics to long time diffusion. Motion of a node in a tethered membrane exhibits multi-scale dynamics much richer than that of a chain and provides a detail insight into the in-plane segmental dynamics characteristics of the wrinkle modes to long time diffusion. Such investigation requires in-depth analysis[7] with quality data to probe and identify multi-scale trends[6] in segmental dynamics and structural relaxation. For example, the mean square displacement of the center node of the sheet with the time step shows well-define modes from short to long time regimes (see Figure 4, 5). From Figure 4, we can recognize three types of power-laws dynamics in sequence: (*i*) short time dynamics, $R_n^2 \propto t^{2v1}$ with $v_1 \sim 1/6$ followed by (*ii*) a faster dynamics $R_n^2 \propto t^{2v2}$ with $v_2 \sim 1/3$ before slowing down substantially, $R_n^2 \propto t^{2v3}$ with $v_3 \sim 1/10$. Although a closer examination of the data in Figure 4 ($t \sim 10^7$) shows the onset of diffusive behavior in the long time despite large fluctuations (see the inset Figure), the large-scale simulation (Figure 5) clarify it with much better accuracy. These multi-scale segmental dynamics are unique characteristics of propagating modes of a tethered membrane, very different from those in a chain. Thus, we find that the local modes propagate via multiple scale dynamics (v_1, v_2, v_3) with well-defined crossovers. Further, the type and range of the multi-scale dynamics depends on the type of sheet (ε_{nn}) and underlying matrix in which it is embedded.
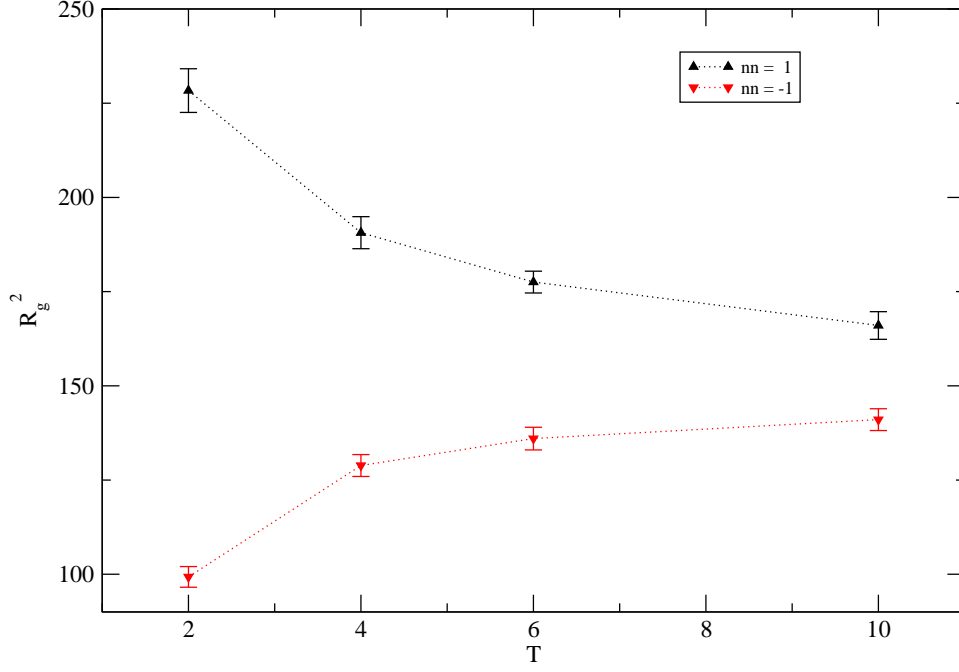
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Figure 3. Variation of the radius of gyration with the temperature of the sheet (16²) on a 64³ lattice with the node-node interaction *nn = -1, 1* and node-solvent interaction *ns = -0.5*. Ref. [5,6].
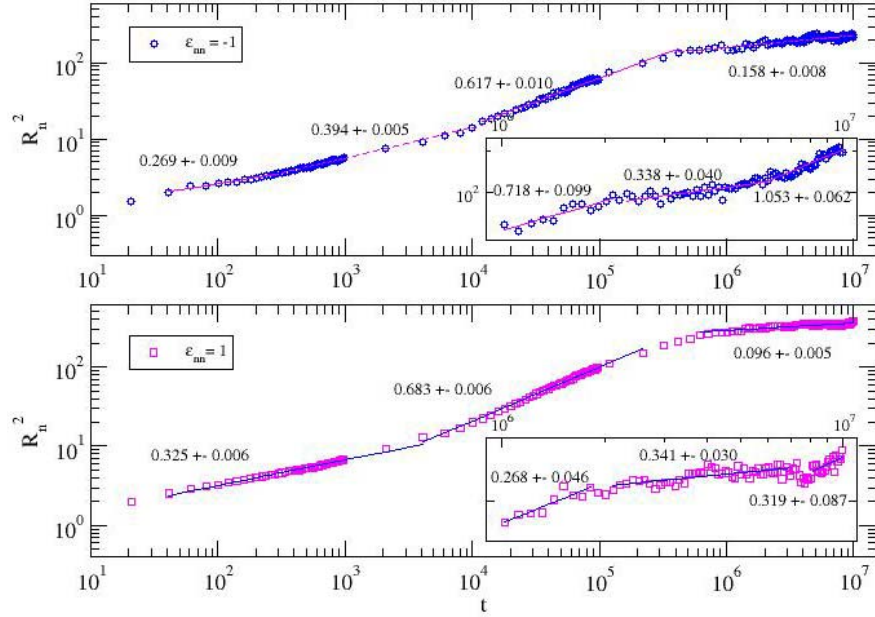

Figure 4. Variation of mean square displacement of the center node (R_n^2) with the time step *t* of the membrane of size *64²* on a *200³* lattice at time steps with interactions ε_{nn} = -1, 1 and ε_{ns} = -0.5 and *T=2*; *10-1000* independent samples are used ref[6].
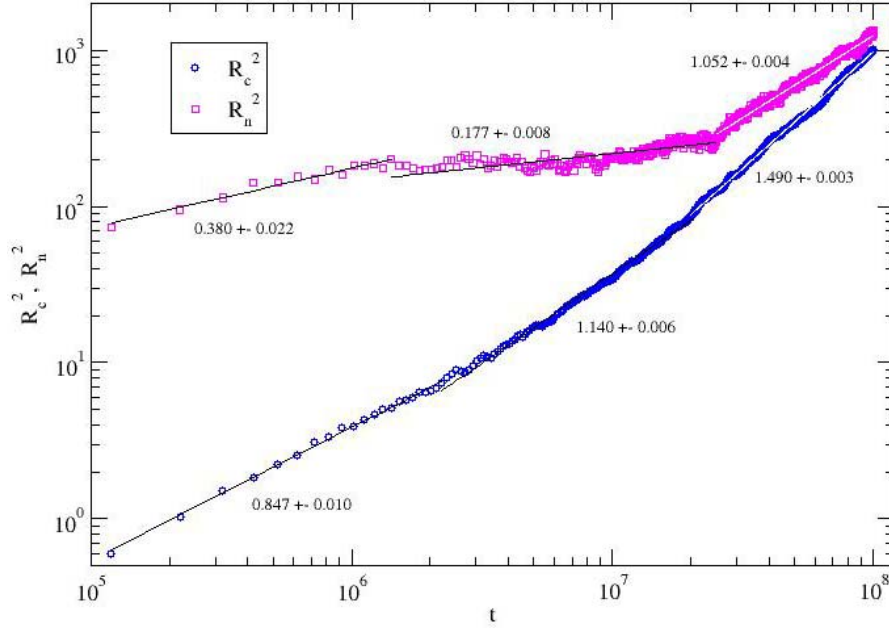
Figure 5. Variation of mean square displacement of the center of mass (R_c^2) of the membrane of size *64²* and that of its center node (R_n^2) with the time step *t* on a *200³* lattice at time steps with interactions ε_{nn} = *-1* and ε_{ns} = *-0.5* and *T=2*. 50-100 independent samples are used.

Dispersion of the layer of platelets

Layer of clay platelets is common in clay nano-composites but their uniform dispersion in a composite matrix is highly desirable to achieve optimal performance. Thus, understanding the dispersion of clay platelets in crucial in understanding how to control their distribution – a very difficult issue to achieve in laboratory sample. This is also a challenging issue by computer simulations, as it takes enormous amount of time to exfoliate a stack of sheets with off-lattice computer simulation[8]. Therefore, an accelerated computational method particularly in modeling for sheets is essential – the coarse-grained model for sheet described above sets the basis for following investigation on dispersion and exfoliation of stacked platelets[9]. The underlying lattice structure provides the simplicity and computational efficiency while providing ample degrees of freedom for nodes to move and for sheet bonds to fluctuate. As a result we are able to carry out extensive computer simulations studies[9] and draw meaningful conclusion on effects of temperature, platelet size, and quality of solvent on the exfoliation of stacked sheets. In the following we briefly describe the dispersion of platelets in (a) effective solvent media, (b) explicit solvent, and (c) polymer matrix.

(a) Effective solvent

We consider a layer of stacked sheets (four) with a small interstitial separation (4 lattice constant); the empty lattice sites represent effective solvent medium. We know that raising the temperature enhances the mobility. As a result the exfoliation of platelets is enhanced which can be verified a result d from the visualization[9]. A quantitative manifestation of the exfoliation can be verified from the changes in the transverse component (y-component normal to initial planar configuration of the layered sheets) of the radius of gyration (R_{gy}) among other quantities such as mobility. Figure 6 shows clearly that R_{gy} increases more rapidly on raising the temperature.
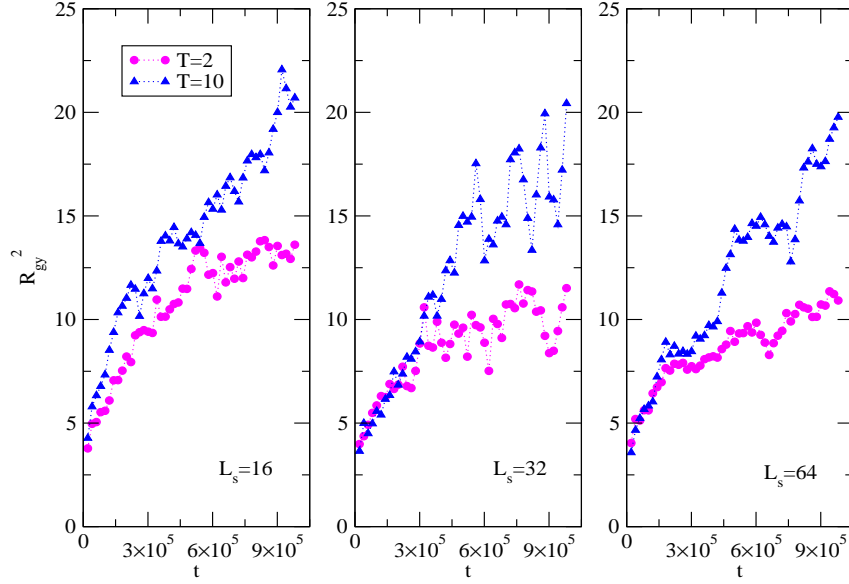
Figure 6. **Transverse component of the mean square radius of gyration of each platelet in the stack of 4 at T = 2 and 10 with the node-solvent interaction ε = -1. ref. [9].**

Since the relaxation of the sheet depends on its size, our simulations[9] show that exfoliation is enhanced on decreasing the size of platelets. Quality of solvent plays a critical role in exfoliation of the sheets. Interaction between nodes and the solvent site control the quality of the solvent and can be varied, e.g., an attractive interaction ε = -2 to a repulsive interaction ε = +2 within a range of interaction r.

(b) Explicit solvent

Attempts are made to understand the dispersion of layered platelets in presence of solvent that can be identified explicitly. Although the effective solvent medium represented by empty lattice sites is effective and efficient, it is difficult to identify mobility, fluctuation, and correlations. Representing the solvent by particles (each with the same size as the node of the sheet) could be a viable approach. Unlike each empty lattice site representing the characteristics (interaction) of the fluid in effective solvent medium approach, only a fraction (p_w) of lattice sites are occupied by explicit solvent particles. A layer of platelets is immersed in lattice with solvent of concentration p_w. Interaction between solvent and nodes of the sheets can be treated in a similar fashion as described above with effective solvent medium. However, both solvent constituents and clay platelets can perform their stochastic motion independently; the interaction between solvent and platelets may lead to their spatial distribution. In addition to dispersion of platelets, one can investigate the intercalation of the solvent constituents in interstitial spacing between the layered sheets. Thus, intercalation of solvent and exfoliation of layered platelets can be examined as a function of temperature, quality of the solvent and its concentration; extensive computer simulations are performed[10] to investigate these issues.

Figure 7 shows snapshots to illustrate the effect of the quality of solvent on the dispersion of the layered platelets. The attractive interaction between solvent and the sheets ($\varepsilon = -2$) at the temperature $T = 1$ leads to enormous intercalation of solvent particles between the interstitial platelet layers. The interstitial solvent particles tend to hold the platelets so strongly as to cease their dissociation. Reducing the interaction strength (($\varepsilon = -1$) reduces the layer cohesion and sheets begin to disperse.
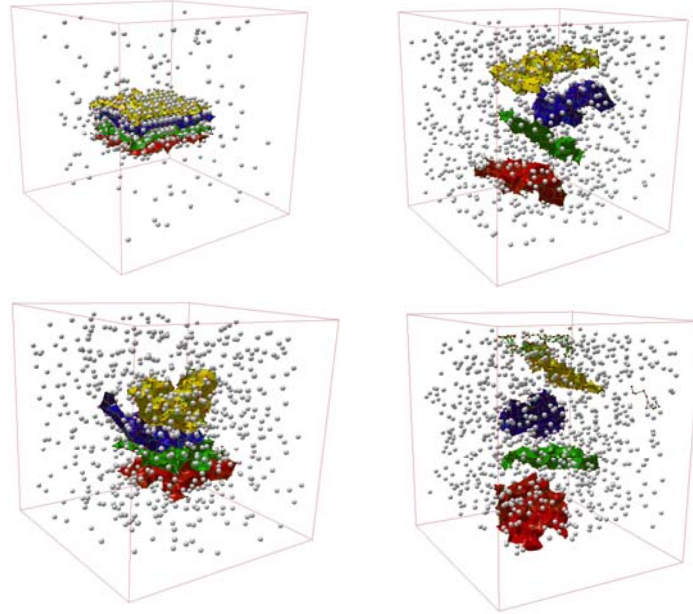

Figure 7. Snaps of stacked platelets (each of size 16^2) after 10^6 time steps on 64^3 lattice with clay-solvent interaction $\varepsilon = -2$ ($T = 1$, left top, $T=5$ right top), $\varepsilon = -1$ (T=1, left bottom), $\varepsilon = 1$ (T=1, right bottom). Solvent particle concentration is 0.2. ref. [10].

Changing the quality of solvent to a repulsive interaction ($\varepsilon = 1, T=1$) causes the platelets to fully exfoliate. Dispersion of layered sheets is also enhanced by raising the temperature ($T=5$) even with attractive solvent ($\varepsilon = -2$). Note the contrast in the effect of solvent on dispersion from effective solvent media to explicit solvent. While the repulsive interaction reduces dispersion in effective medium (phobic effect), it enhances the dispersion with explicit solvents (philic effect) due to intercalation and stochastic pulling of sheets by solvent. The contrast may be somewhat misleading as the concentration of explicit solvent is much lower than that of the effective medium where each empty site acts as a solvent. However, one may still use the empty sites to represent an effective solvent in addition to particles and sheets with a three component systems – this increases our parameter space and could be interesting future projects.

Efforts are made to quantify above observations by analyzing the density profiles and mobility of solvent particles and sheets, and their radius of gyration[10]. Figure 8 shows the density profile of solvent particles and sheets to show the effects of temperature on dispersion of both sheets and solvent particles. Clearly the cohesion and dispersion of sheets and solvent is verified at lower temperature (T=1). At higher temperatures, dispersion become dominant and the layering and structural patterns smeared out. The above conclusions are thus verified by other quantities as well[10].
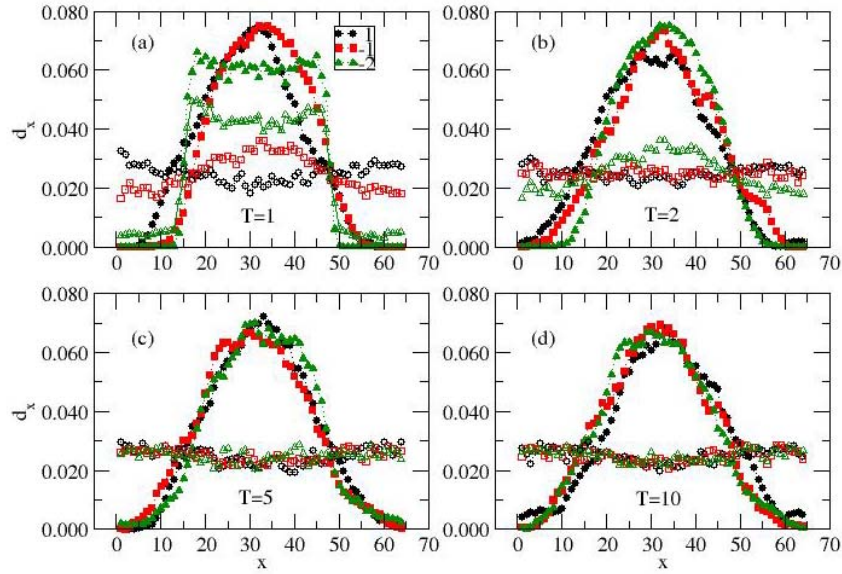

Figure 8. Transverse planar density (dx) of clay (filled) and solvent (open) particles versus x at T = 1-10 with clay-solvent interact ε = 1, -1, -2. A stack of four platelets each of size 162 is used on a lattice of size 643 each with 10 independent runs. Ref [10].

(c) Polymer chain matrix

The above studies are extended further by incorporating mobile polymer chains as the underlying matrix for the layered sheets to disperse in. The polymer chain is modeled by tethered nodes, a bond-fluctuating chain model. The parameters include polymer-clay interaction, concentration of polymers, their molecular weight, temperature, etc. We have carried out an initial investigation[11] on the effects of interaction and molecular weight on the dispersion of layered platelets. Figure 9 a snapshot summary to illustrate our observation.
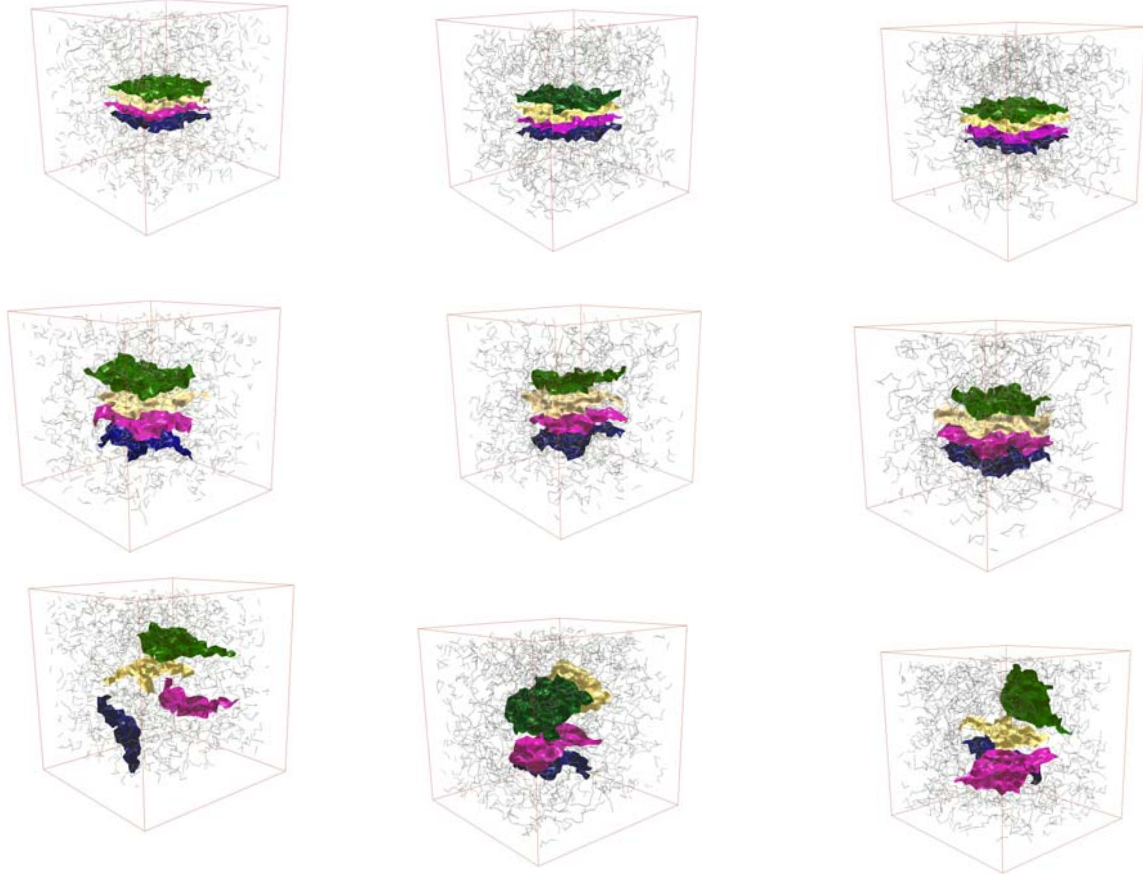
Figure 9. Snapshots of the platelets in mobile polymer chain matrix. Top row is the initial configurations. The polymer chain length L_c = 4 (first column), 16 (second column), 64 (third column). Interaction between polymer and sheets ε = -1 (second row) and ε = 1 (third row). Sheets of size 16^2 are used on a 64^3 lattice at temperature T = 1 with the range of interaction r^2 = 8. Each configuration is final after 10^6 time steps with the polymer chain concentration p_c = 0.1.

Polymer chain matrix, though more complex than the effective medium and explicit particles matrix, provides a more realistic feature in modeling nano-clay composites. Not only is the polymer-clay interaction important in understanding the dispersion of layered sheets but also the heterogeneity caused by entanglement and relaxation of the host matrix. From the visual analysis of the snapshots, one can draw some preliminary conclusions as follows. The repulsive interaction between the polymer chains and the clay platelets enhances dispersion while the attractive interaction suppresses it. This is somewhat similar to the effect of explicit solvent particles matrix at least for the polymer matrix with low molecular weight. Entanglements of the polymer chain occur on increasing their molecular weight. The relaxation time for matrix to re-arrange becomes relatively long with high molecular weight polymer chains – the local structures result in configuration in which platelets are embedded in effective caged network of mobile polymer chains. Thus, the entanglement of polymer chains at higher molecular weight suppresses dispersion – an entropic trapping. Interaction driven thermodynamics dominates in a polymer matrix with low molecular weights (as in explicit solvent particles matrix) where dispersion depends on the interaction (type and strength). The entropic trapping prevents exfoliation in a polymer matrix with large molecular weight. Understanding the dispersion

becomes very complex in the intermediate regime where interaction and entanglement are comparable.

Biopolymers

Hybrid systems are becoming increasingly important in designing materials with optimal characteristics with the continued growth in understanding the fundamental properties of bio-molecular and cellular systems. Bio-materials offer high potential to enhance the desirable characteristics. Proteins are some of the most versatile bio-polymer and can be incorporated in hybrid materials to achieve high performance. In this regard, some attempts[12] are made in modeling a polymer chain with specific sequence of amino-acid groups. Unlike a homo-polymer chain, each node is a coarse-grained description of amino-acid group in the bond-fluctuation model where all of the 20 amino acid residues are broadly divided into three groups, hydrophobic (H), polar (P), and electrostatic (E). Using a specific protein, aspartic acid protease (see Figure 10), we are able to describe conformations and dynamics in effective solvent matrix.
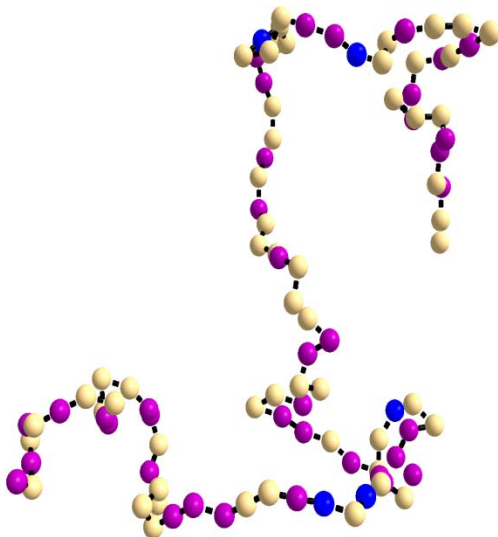

Figure 10. A coarse grained description of aspartic acid protease (1DIFA) with H (pink), P (gold), and E (blue). Ref. [12].

The dynamics of the aspartic acid protease chain is examined by analyzing the variation of the RMS displacement of the center node of the chain and that of its center of mass as presented in Figure 11. A systematic change in dynamics from short time to long time regime is clearly seen[12] on increasing the strength of the solvent interaction.
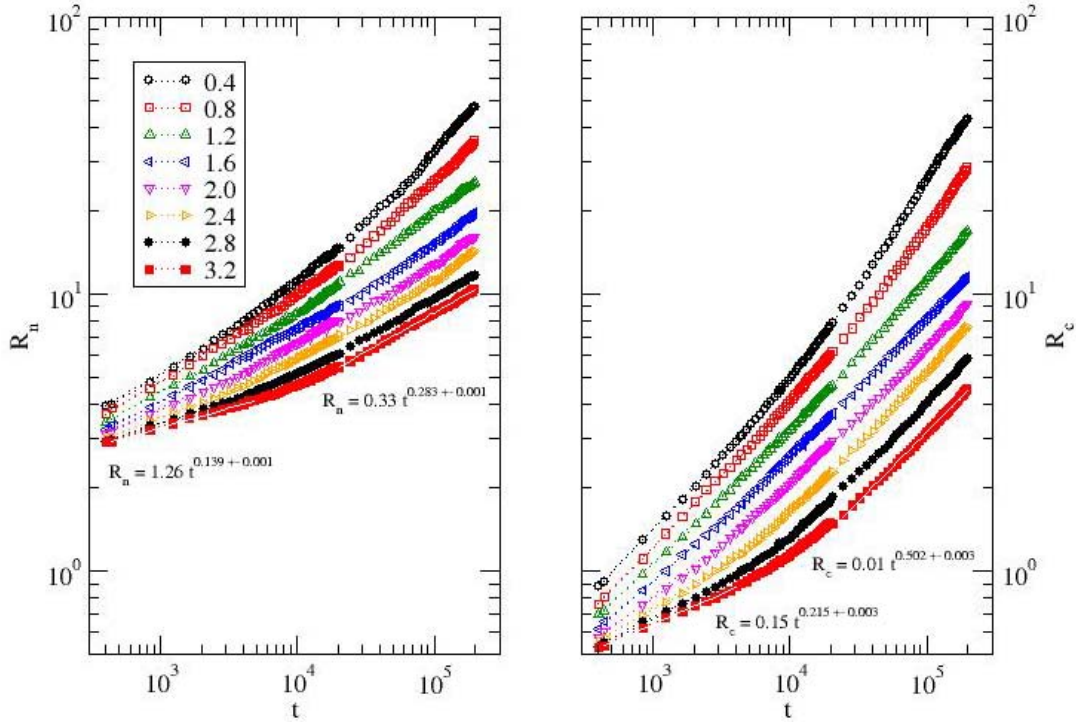
Figure 11. Variation of the RMS displacement of the center node (R_n, left) of aspartic acid chain and that of its center of mass (R_n, right) with the time step t for various solvent media characterized by the interaction strengths ($\varepsilon = 0.0 - 3.2$). Lattice size 60^3 with 50-2000 independent samples is used in each solvent medium. Ref. [12].

Conformation of the chain is also analyzed in detail, particularly the dependence of the radius of gyration on the solvent strength as presented in Figure 12. Chain expands or swells, i.e., the radius of gyration increases on increasing the solvent interaction strength. Further, the expansion is linear with the interaction strength in relatively weaker solvent interaction regime and nonlinear at higher interaction strengths. Insets in Figure 12 show the variation of the radius of gyration (R_g) of the chain and its end-to-end distance (R_e) in the long time regime in a relatively strong solvent medium. The oscillatory behavior of R_g and R_e seems to suggest that chains contract and expand (a earth-worm motion) over the time scales that depend on the quality of the solvent. These studies provide an insight into how to incorporate a protein chain in composite and investigate its interaction with the clay surface.
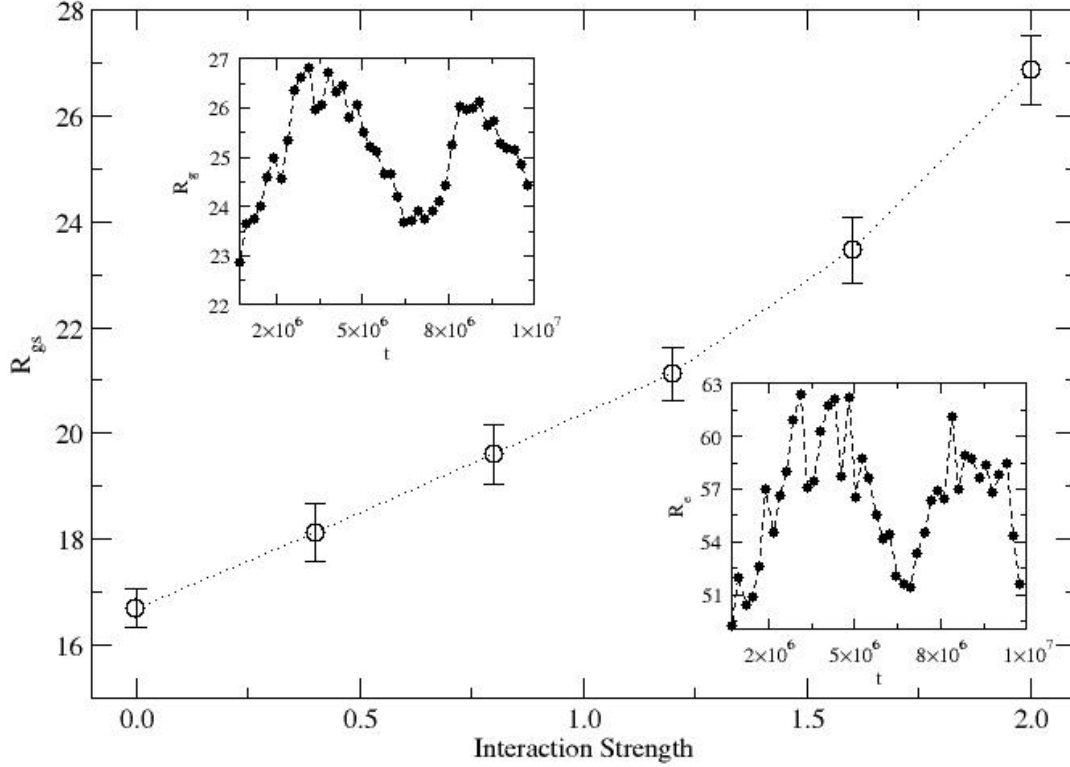
Figure 12. Equilibrium radius of gyration (R_{gs}) versus interaction strength. Inset shows the variation of the radius of gyration (R_g) of the aspartic acid chain and its end-to-end distance (R_e) in the long time regime for the solvent interaction ($\varepsilon = 3.2$). Ref. [12].

Ongoing efforts and outlook

Although this is a report at the end of a productive research under-taking, it stimulates enormous amount of important issues to probe by extending these investigations. Some of these are pointed below briefly.

1. Effect of rigidity of the platelet on the conformation and dynamics of sheet, and dispersion of layered platelets.

2. Effective solvent is an efficient and effective approach but exhibits opposite effects of explicit solvent particles matrix. Studying the dispersion of layered platelets in effective solvent and explicit solvent particles (combined), a three component systems would be interesting.

3. On a long term it would be worth exploring the dispersion and exfoliation of layered platelets and intercalation of constituents of the multi-component host matrix, e.g., particles, polymer chains, effective solvent matrix.

4. Incorporating protein chains in these systems would be highly desirable.

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